

Effect of Temperature on Porosity of Dried Whole Milk Powder Granules

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Abstract

Densities of spray-dried whole milk foam were measured at 25, -80, and -195 C by pycnometric techniques, using He or N₂ as the displaced medium. Evidence was obtained for marked thermal contraction of the powder particles at the lower temperatures, with associated closing of the pores on the powder surface. These effects were manifested in decreased rates of diffusion of the gases to the interior of the powder particles as the temperature was lowered.

As a result of a series of studies on the physical nature of dried food particles, utilizing gas displacement techniques, we have reported that various milk powders (3) and certain freeze-dried foods (5) contain a microporous structure capable of curtailing rapid diffusion of gases to the interior of the dried particles. These studies were confined to the displacement of He, N₂, H₂, and air by the dried materials when held at 25 C. In the present study we have investigated the effects of thermal contraction upon the pore structure of dried whole milk powder granules. In particular, data are reported pertaining to the diffusion of He and N₂ into foam-spray-dried whole milk powder particles when held at -195, -80, and 25 C.

Materials and Methods

The foam-spray-dried whole milk powder used in the present study was produced in the Dairy Products Laboratory pilot plant according to the method of Hanrahan et al. (10), using a 2.7-m Swensen spray dryer modified to inject high-pressure nitrogen gas into the feed prior to atomization. The volume of N₂ injected was 125 liters per kilogram of 50% concentrate.

All the gases used were purchased from the Southern Oxygen Company. The He was purified by passing through a charcoal trap maintained at -195 C, previously degassed at 250 C. Prepurified N₂ was used after passing through a liquid nitrogen trap to remove any traces of moisture.

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In these gas displacement studies, an all-glass custom-made volumetric adsorption apparatus was used for the volume measurements, as previously described (3), but with the sample tube containing the powder maintained at three different temperatures. Measurements at 25 C were made with the sample tube held in a constant-temperature water bath capable of maintaining uniform temperatures within a range of ± 0.02 C. Water from this bath was circulated through the gas burette, to maintain the temperature of the entire system constant for the measurements made at 25 C. Volume determinations at -80 C were carried out with the sample tube immersed in a dry ice-acetone bath. A platinum resistance thermometer was used to measure the temperature of this bath. Measurements at -195 C were made with the sample tube immersed in a liquid nitrogen bath, with the temperature observed in this case with a nitrogen vapor pressure thermometer.

In all cases suitable gas law equations were used to calculate the sample volumes after appropriate calibrations of the system were made employing empty sample tubes.

Results

Values for the density of the foam-spray-dried whole milk powder, as determined under the described experimental conditions, are presented in Table 1. With helium at -80 C and nitrogen at 25 and -80 C, gas pressure in the system did not remain constant during the volume determination, but exhibited a slow de-

TABLE 1
Density of foam-spray-dried whole milk powder in grams per cubic centimeter

Displaced gas	Helium	Nitrogen
Temperature (C)		
25.1	1.26	0.97 ^a 1.25 ^b
-80.2	0.99 ^c 1.17 ^d	0.84 ^e 1.03 ^f
-195.7	0.47	

^a Initial value at P = 875.5 mm Hg.

^b Value at P = 853.9 mm Hg after 6.3 hr.

^c Initial value at P = 694.1 mm Hg.

^d Value at P = 680.2 mm Hg after 2.8 hr.

^e Initial value at P = 705.3 mm Hg.

^f Value after 2.5 hr.

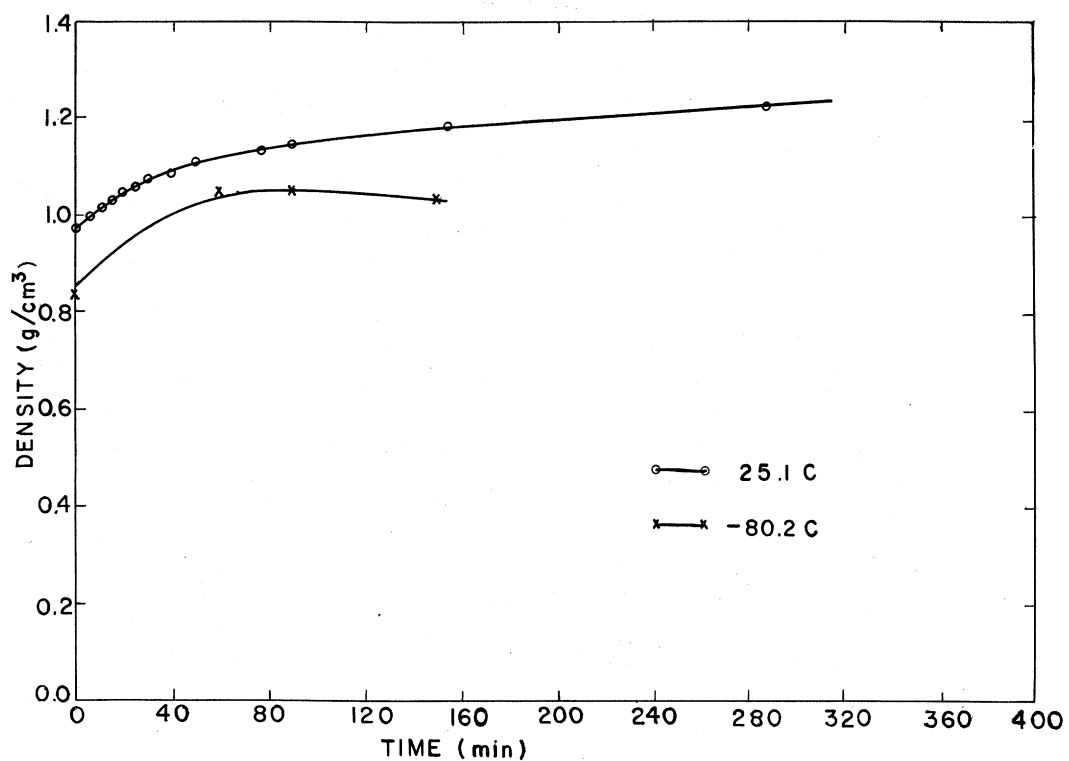


Fig. 1. Variation in density of foam-spray-dried powder with time, using He as the displaced gas.

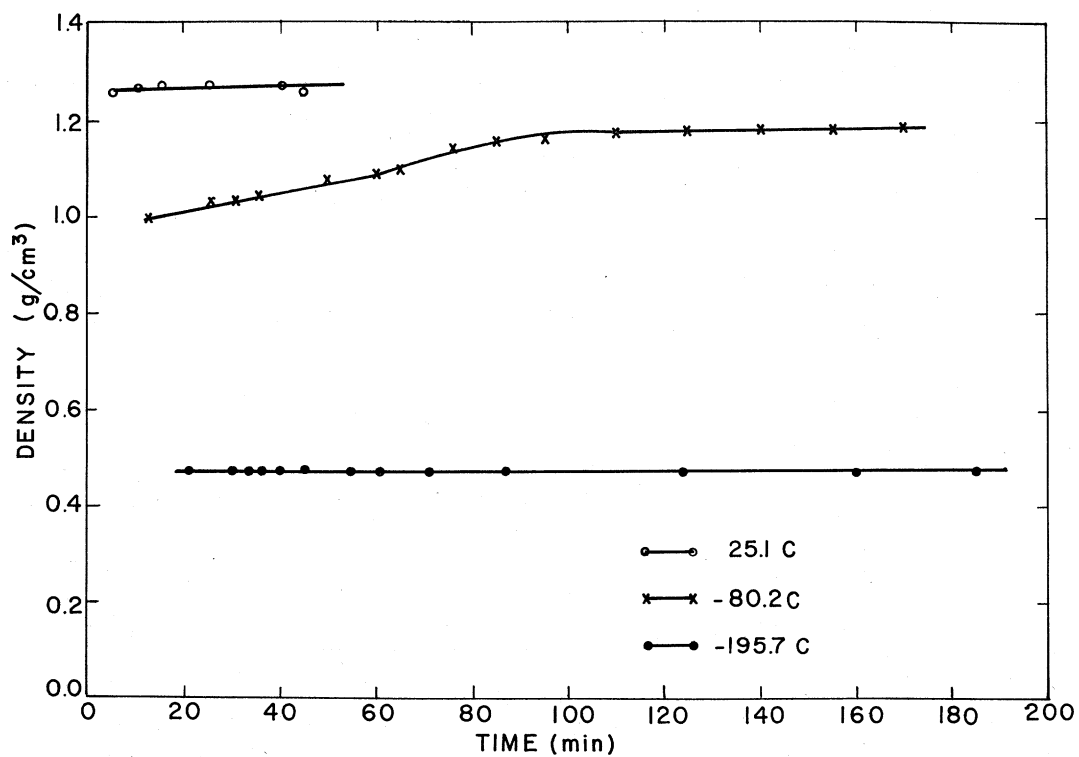


Fig. 2. Variation in density of foam-spray-dried powder with time, using N₂ as the displaced gas.

crease with time. This means that there is a slow increase in the volume of gas required to fill the void space in the sample and, accordingly, there is a slow creep or increase in the apparent density of the solid material with time. This behavior is demonstrated in Figures 1 and 2, where we have plotted the density in grams/cm³ against time in minutes for each set of experimental conditions.

These results may be explained in terms of the restricted passage of the gas molecules through the narrow capillaries present in the powder mass, as these passages are of molecular dimensions. When the powder was held at 25°C there was no restriction in diffusion of the He molecules to the interior of the powder granules; however, the entry of the larger N₂ molecules was impeded. At -80°C there was sufficient thermal contraction of the particles to seal off some of the surface pores, resulting in hindered diffusion for both He and N₂, and accordingly lowered apparent density values were observed. At -195°C all the surface micropores were sealed off, resulting in a much lower density value as determined with He displacement. There was no apparent creep in the density with time at this temperature.

Discussion

Results reported in the present study tend to confirm our previous conclusion (3, 6), that foam-spray-dried whole milk powder particles exhibit molecular sieve behavior. Densities determined by helium displacement are usually considered as true densities, because the helium is able to fill all the voids between the particles, as well as any pore space due to cracks, crevices, etc., internal to the particles. This property was observed at 25°C; however, at the lower temperatures only apparent density values were obtained with He. Since the surface openings are of molecular dimensions, it is quite reasonable that the thermal contraction of the powder at the lower temperature should be effective in sealing off these openings.

Mervyn Jones (11, 12) has treated the problem of flowthrough pores of molecular dimensions in terms of an equation involving three types of flow: Poiseuille, Knudsen, and surface flow in an adsorbed layer. When the pore diameter is of the order of the He or N₂ molecule, the terms in Mervyn Jones's equation corresponding to Poiseuille and Knudsen flow, respectively, are negligible, and surface flow will predominate.

Flow of this type should require a considerable energy of activation for the molecules of the diffusing species to squeeze through such nar-

row capillaries (1). Data reported in this paper are in agreement with this predicted behavior.

The reported thermal effects upon the pore structure may be further visualized in terms of the molecular sieve behavior of certain synthetic zeolites as discussed by Dubinin et al. (9). Zeolites are a rare example of porous adsorbents with rigid aluminosilicate frames for which the shape, dimensions, pore interrelation, and surface nature are known from independent X-ray diffraction data. These zeolites contain various-sized cavities interconnected by means of 6-, 8-, or 12-membered oxygen windows, with respective diameters of 2.5, 4.2, and 8-9 Å (2). The accessibility of the primary porous structure of the zeolites to adsorbed molecules is then governed by the critical diameters of these molecules and the effective diameters of the windows. Molecules of substances having critical diameters substantially smaller than the windows leading into the zeolite cavities are usually adsorbed well and rapidly by the dehydrated zeolite crystals. As the molecular diameter approaches that of the windows, the adsorption rate falls off considerably, and the process of diffusive transfer of molecules to the primary porous structure is characterized by an ever-increasing activation energy. As a result, a strong temperature dependence of adsorption rate is manifested which, in limiting cases, leads to practical inaccessibility of the primary pore structure of the dehydrated zeolite crystals at low temperatures. Breck et al. (8) reported that at -78°C carbon monoxide, nitrogen, and argon are adsorbed by Zeolite A in the sodium ion-exchange form in appreciable quantities and relatively rapidly. At -195°C, however, the extent of adsorption, even over long periods, is extremely low. For substances with larger molecules, the windows leading into the large cavities are inaccessible and adsorption can occur only on the external surface of the zeolite crystals. The amounts so adsorbed are incomparably small in relation to the amounts adsorbed of substances for which the primary porous structure is available.

Dubinin et al. (9), therefore, concluded that the fine selectivity of the zeolites for adsorption may be due to the molecular sieve effect, and also to the sharp differences in adsorption kinetics caused by the activation energy of the intradiffusive transfer of adsorbed substances into the primary pore structure. Such a mechanism may very well explain our results with foam-spray-dried whole milk powder. The observed thermal effects may also be related to the low values for milk powder surface areas

as calculated from N_2 (4) and Kr (6) adsorption data obtained at -195°C .

In a comparative study of the rates of oxygen removal from milk powders by nitrogen flushing and vacuum degassing, it was found that the efficiency of the operation was drastically diminished when the milk powder was held at -195°C (7). These results may also be understood in terms of the effective closing of the pores due to thermal contraction, as well as the requirement for sufficient activation energy for surface flow.

Since surface flow is the predominant mode of transport in this system, increased flushing efficiency would be expected at -195°C , since more N_2 is adsorbed at this temperature and surface flow depends upon concentration of adsorbed material. This anticipated enhanced efficiency was, however, not observed (7). On the basis of the present study we are able to conclude that at -195°C there is sufficient thermal contraction to effectively seal the narrow surface openings and completely prevent gas diffusion to the interior of the powder particles.

On the basis of the present study it seems likely that the effects of temperature upon the pore structure of milk powder particles should be considered in choosing the optimum temperature for packaging dried whole milk powder so as to prevent the occlusion of oxygen. These effects may not, however, be observable over the limited temperature available for commercial packaging operations.

References

- (1) Barrer, R. M. 1941. *Diffusion in and Through Solids*. Cambridge University Press, Cambridge, England.
- (2) Barrer, R. M., Bultitude, F. W., and Sutherland, J. W. 1957. Structure of Faujasite and Properties of Its Inclusion Complexes with Hydrocarbons. *Trans. Faraday Soc.*, 53: 1111.
- (3) Berlin, E., and Pallansch, M. J. 1963. Influence of Drying Method on Density and Porosity of Milk Powder Granules. *J. Dairy Sci.*, 46: 780.
- (4) Berlin, E., Howard, N. M., and Pallansch, M. J. 1964. Specific Surface Areas of Milk Powders Produced by Different Drying Methods. *J. Dairy Sci.*, 47: 132.
- (5) Berlin, E., Kliman, P. G., and Pallansch, M. J. 1966. Surface Areas and Densities of Freeze Dried Foods. *J. Agr. Food Chem.*, 14: 15.
- (6) Berlin, E., Kliman, P. G., and Pallansch, M. J. 1965. Krypton Adsorption on Dried Milk Powders. 150th Ann. Meet., Am. Chem. Soc., 32A. Atlantic City, N. J., September.
- (7) Berlin, E., Rainey, N. H., and Pallansch, M. J. 1965. Relative Effectiveness of Gas Flushing and Evacuation for Removal of Oxygen from Foam-Spray-Dried Whole Milk Powder. *J. Dairy Sci.*, 48: 777.
- (8) Breck, R. W., Eversole, W. C., Milton, R. M., Read, T. B., and Thomas, T. L. 1956. Crystalline Zeolites. I. The Properties of a New Synthetic Zeolite, Type A. *J. Am. Chem. Soc.*, 78: 5963.
- (9) Dubinin, M. M., Bering, B. P., and Serpenskii, V. V. 1964. Physical Adsorption at the Gas-Solid Interface. In *Recent Progress in Surface Science*, Vol 2, pp. 38-42. Danielli, J. F., Pankhurst, K. G. A., and Riddiford, A. C., eds. Academic Press, New York.
- (10) Hanrahan, F. P., Tamsma, A., Fox, K. K., and Pallansch, M. J. 1962. Production and Properties of Spray-Dried Whole Milk Foam. *J. Dairy Sci.*, 45: 27.
- (11) Mervyn Jones, W. 1951. Mobility in a Sorbed Layer. I. The Flow of Gases and Vapors Through Porous Media. *Trans. Faraday Soc.*, 47: 381.
- (12) Mervyn Jones, W. 1952. Mobility in a Sorbed Layer. II. Surface Flow Through Pores of Molecular Dimensions. *Trans. Faraday Soc.*, 48: 562.